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THE CATALYTIC DECOMPOSITION OF ETHYL ACETATE BY MEANS
OF ALUMINUM OXIDE

BY

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A THESIS SUBMITTED FOR
THE DEGREE OF MASTER OF ARTS

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INTRODUCTION

The velocity of a great number of chemical reactions may be modified by the presence of a substance which, after the completion of the reaction, has the same chemical composition as at the beginning. Such a substance is usually called a catalyst. An innumerable number of reactions are subject to catalytic influences. Ostwald says: "There is probably no kind of chemical reaction which cannot be influenced catalytically, and there is no substance, element, or compound which cannot act as a catalyser." (Zeit. Elektrochem. 7, 995(1901); Nature, 65, 522(1902)).

Catalytic phenomena have been variously classified according to the particular view which is taken of the mechanism of the reaction. It is very convenient to take the classification which divides catalytic reactions according as the components of the system are in the same or in different states of aggregation. Thus, heterogeneous, or contact catalysis, is considered to be the reaction in which the catalyst is in a different state of aggregation from the substances which are undergoing reaction. Homogeneous catalysis is the reaction in which the catalyst and the reacting substances are in the same state of aggregation.

There have been many theories advanced for the explanation of the action of catalytic agents. Perhaps it would be well to review the most important of these theories. In

most cases there has been obtained no definite and accurate information as to the actual mechanism of the chemical reaction which takes place. The theories brought forth are based on rather insufficient evidence or on vague ideas.

The intermediate compound theory offers a simple interpretation of many catalytic processes. Some believe that the action of platinum on a mixture of hydrogen and oxygen is due to the formation of intermediate oxides of platinum which are subsequently reduced by hydrogen. (Brodie; Phil. Trans. 151, 855 (1862); De la Rive, Pogg Ann. 46, 489 (1839); Wohler, Zeit. anorg. Chem. 29, 1 (1901). Sabatier and Senderens came to the conclusion from their long investigations on metallic catalysts that there were formed unstable hydrides of the metals which, in turn, reduce the organic compounds.

(Die Katalyse in der organischen Chemie, 240 (1914)

According to the same authors, oxides owed their catalytic action to the temporary formation of various unstable compounds of the catalytic agent with the reacting substances or one of the reaction products. Henderson, also, assumes intermediate compound formations, but he gives no evidence for the foundation of his belief. (Catalysis in Industrial Chemistry (1919) 4) Ostwald gives the opinion that the assumption of intermediate products is not based upon accurate knowledge of the reactions in question, and it is not proved that the direct reaction takes place less rapidly than the total of the hypothetical intermediate reactions. He has the opinion that all theories are worthless as long as no accurate data exists.

Faraday can be taken as the originator of the adsorption theory. (Mellor; Chemical Statics and Dynamics 259 (1904)) In his study on combustion of gases in the presence of platinum, he supposed that the gases were more concentrated next to the metal and the molecules of the gases were in closer contact. The reaction, consequently, takes place at a greater velocity at surface of the metal. Rideal says that, "the conception that adsorption is the primary action in all cases of heterogeneous catalysis is the viewpoint now generally adopted." (Trans.Am.Electrochem.Soc.,36,149 (1919)) Since alcohol is decomposed into ethylene and water in the presence of alumina and alumina adsorbs water strongly, Bancroft assumes the selective adsorption determines the reaction. (Bancroft, Journ. Phys. Chem., 21,573, (1917)) However, he is at a loss for an explanation as to why alumina decomposes alcohol in the presence of a large amount of water vapor. Bancroft has arrived at the conclusion that only those substances which are absorbed by a solid are catalyzed by it. While the catalytic action of solids may be solely the result of the increased surface concentration in some cases, it is not the only factor. As a result of selective adsorption, different reaction products result with different catalytic agents. A catalytic agent tends to produce the system which it absorbs the most strongly. (Bancroft: Jour.Phys.Chem.,21,676 (1914))

The electrochemical catalysis theory has been supported by Langmuir, Harkins, and Marcelin.

(Langmuir; J.Am.Chem.Soc.38, 2221(1916);39,1848 (1917);40,1361 (1918)
Harkins; J.Am.Chem.Soc.,39,541 (1917)

Marcelin; Ann.Physik, 1,19 (1914)

Langmuir suggests that in the case of fatty acids floating on water an oriented adsorption takes place. There is evidence that the carboxyl groups are selectively held by the water. He believes the adsorbed film is bound to the adsorbing surface by unsatisfied valencies of the adsorbent. Applying Langmuir's conception to the case of ethyl acetate, it might be said that it suggests the possibility that with different catalysts, the methyl group may be adsorbed by one, the ethyl group by another, and the carboxyl or carbonyl group by still another. His theory may be best summarized by saying that the forces involved in adsorption, surface tension, etc., do not differ greatly from the forces causing the formation of chemical compounds. (I. Langmuir, J.Am.Chem.Soc., 39,1048 (1917)).

The purpose of the study of the catalytic decomposition of ethyl acetate by alumina was to gain an insight into the possible nature of catalytic action. Alumina breaks up ethyl alcohol into ether and water, and ethylene and water. Acetic acid is decomposed into acetone and water. It is not known just how the water is formed in these reactions. The investigation of the products from the decomposition of ethyl acetate might possibly indicate the probable mechanism of this type of catalysis.

HISTORICAL

The greatest impetus toward the study of the catalytic decomposition of organic compounds has been given during comparatively recent years by the increasing technical importance of catalytic reactions. Previously, chemical or pyrogenic reactions were used to break down hydrocarbons or their derivatives. A great deal of study on the decomposition of aliphatic compounds by catalysts has been done by Sabatier, Senderens, and Maihle. Investigations have been made also by Ipatieff, Mentschukene, Berchelot, and Pean de Saint Gilles.

The general apparatus used by Sabatier and his co-workers was simply constructed. A straight, hard glass tube about 60 cm in length in which a layer of the catalyst was placed, served as the reaction chamber. The heat was furnished by a gas grill or an electric resistance furnace. The dried vapors of the substances were led over the catalyst and the products of decomposition were passed through a spiral condenser and the gases were collected in an eudiometer. The temperature was obtained by means of a thermometer placed in sand or magnesia beside the reaction tube or placed in the inside of the tube.

Rideal and Taylor modified the apparatus of Sabatier for the investigation of catalytic gas reactions. (Catalysis in Theory and Practice (1919) 72). A vertical chamber was electrically heated by means of resistance wire. The upper end was tapered to hold a thermometer or thermocouple in the catalyst which was placed in an inner tube. This change permitted

the entering gases to heat^{be} between the two tubes before entering the inner tube, and thus gave an easily regulated temperature.

The study of the effect of catalysts on acids, alcohols, and esters of the aliphatic series has been perhaps the most thoroughly studied of the organic catalytic decompositions. Senderens found that alcohols passed over alumina decomposed to ethylene hydrocarbons. Ipatieff believed that as the complexity of the alcohol increased, the temperature necessary for catalysis also increased. However, Senderens proved that in his investigations of action of alumina on the alcohols the contrary was true. He found that the temperature of the dehydration of the alcohol decreased with the weight of the molecule. (Senderens; Bull. de Soc. Chem. 1, 75 (1907)) Senderens and Maihle noted that for the same alcohol, the reactions varied with the nature of the experiment. Elevation of the temperature increased the rate of reaction. Amorphous oxides were found to be more reactive than crystalline. (Sabatier; Comptes Rendus 147, 106 (1908))

The alumina which was prepared by calcination of an ammonical alum or aluminum sulphate was not as reactive as that made by the precipitation from a salt. Sabatier believed that the dehydration of the alcohol takes place through a formation of an oxide or ether of the alcohol to form an unsaturated hydrocarbon.

Engeler found that the decomposition of ethyl alcohol over alumina was 18 per cent at 380° and 94.15 per cent at 490°. At 210°, diethyl ether resulted. By introducing water

vapor, the rate of decomposition was greatly decreased. (Engelder; J.Phys.Chem., 21,676 (1917). The alumina which was prepared by precipitation from aluminum nitrate apparently retained its activity indefinitely.

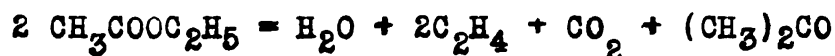
Senderens passed methyl alcohol over alumina and obtained dimethyl ether. (Senderens; Bull.de Soc,Chem.,V,480 (1909) With propyl alcohol, propylene was formed, which condensed to diisobutylene.

Senderens noticed that aliphatic acids with alumina decomposed to form ketones. Mixed acids formed mixed ketones. (Senderens; Bull. de Soc. Chem. V, 128 (1909) An aldehyde was obtained if formic acid was used with another fatty acid. As the complexity of the acid increased, the efficiency of the catalyst decreased. Acetic acid with alumina gives as products, acetone, carbon dioxide and water. Senderens, upon heating acetic acid alone at 460° , found no decomposition occurred but with alumina at 350° , he obtained 90 per cent carbon dioxide and almost pure acetone. He believed that the acetone was derived from acetic anhydride, which was formed from the acetic acid as an intermediate compound. Higher acids gave ketones in a like manner.

Sabatier and Maible studied the action of different metallic oxides as catalysts upon aliphatic esters. (Sabatier and Maible, Bull.de Soc. Chem.VII, 504 (1910) They found the decomposition varied with the oxide used. On this basis they divided the oxides into three groups:

- (1) The catalysts decomposing the ester into a ketone, carbon dioxide, water and an olefine.
- (2) A group reacting like thoria giving carbon dioxide, an olefine, an alcohol, and a ketone.
- (3) Another group which splits off an olefine from the ester and leaves an acid.

Senderens found that alumina heated in direct contact with ethyl acetate gave a liquid consisting of water and acetone and gas of 32.5 per cent carbon dioxide and 66.2 per cent ethylene. (Senderens; Bull. de Soc. Chem., III, 802, 823 (1908) Ethyl acetate passed over alumina at 350° decomposed according to the following equation:



The ester alone at 430° was unchanged.

(Senderens; Comptes Rendus, 146, 1211 (1908)

APPARATUS

The general method of investigation was to pass the heated vapors over the hot catalyst and to collect the resulting gaseous and liquid products. The ethyl acetate was passed from a 50 cc burette directly through a capillary U-tube. The end of the U-tube extended into a hard glass furnace tube about 15 cm so as it could act as a preheater to vaporize the ethyl acetate. The furnace tube was approximately 3 cm wide and 48 cm long. A hard glass tube, 1 cm wide and 42 cm long, with a tapering end for the outlet was inserted into the furnace tube to hold the catalyst. The rubber stopper prevented the catalyst tube from touching the walls of the furnace tube. A nitrogen thermometer was placed with the bulb into the center of the catalyst. The stem projected through a rubber stopper to the outside of the furnace.

The furnace consisted of a nichrome wire wound around an alundum tube which was 4 cm wide and 42 cm long. This was placed into a close fitting alundum tube which was surrounded with a large sheet iron shell packed with magnesia. The temperature of the furnace was controlled by a slide wire rheostat. The current was measured by an ammeter.

The vapors were conducted from the tapered end of the catalyst tube to the bottom of an eight inch test-tube one-quarter filled with large glass beads. The tube was placed into ice water. The gas was led into a gas holder. The

saturated sodium chloride solution in the gas holder was withdrawn as fast as the gas entered so as to keep the pressure constant. A mercury manometer on the gas-holder indicated the pressure of the gas.

Care was taken to keep conditions as uniform as possible. The rate of adding the ethyl acetate was regulated by the stopcock on the burette and by the stopcock controlling the outlet of the salt water of the gas holder.

After the eighth run, a Winkler spiral was used in place of the tube for the condensation of the vapors. This spiral consists of two and one-half spirals, 14 cm across and 1.5 cm in diameter. A glass stopcock was sealed on each end of the spiral. This modification gave a more efficient condensation.

At the end of the eleventh run, many other changes were effected, because the preheater caused the ethyl acetate to vaporize intermittently and incompletely. Also, at times, the gas formed by decomposition was drawn back through the burette. To overcome this, the burette was connected by a stopper to a holder with a capillary tube according to the diagram. The tube extended horizontally through a vessel of boiling water into the furnace.

The furnace tube was discarded. A hard glass tube, 2 cm wide and 42 cm long, with a large capillary tube sealed on the end, was used as the furnace and catalyst tube. An indentation in the tube 3 cm from the capillary tube served as a place for a base metal thermocouple. In the tube was placed a layer of glass wool, followed by a layer of glass

beads. The catalyst was packed loosely around the indentation and backed by a layer of glass wool. A narrow sheet of asbestos was wrapped twice around the tube over the indentation. After the thermocouple was tied in place with copper wire, the tube was placed in the furnace with the catalyst about 4 cm from the end of the furnace. A paste made of asbestos and water was used to pack the tube in the furnace.

The end of the capillary led into an adapter connected to a seven spiral condenser made of small tubing bent on a 2 cm radius. A 100 cc wide mouth bottle acted as a receiver for the distillate. Another seven spiral condenser was connected in series between the receiver and the gas holder. The condenser and the receiver was kept immersed in ice water. The gas holder consisted of a 7.5 liter bottle with a mercury manometer. A three-way stopcock enabled the gas to be collected either in the holder or in a burette.

The thermocouple was connected to a Leeds and Northrup potentiometer, recorder and controller which automatically regulated the electrical heating of the furnace to $\pm 2^\circ$. This instrument was a great improvement over the hand control.

It was thought that it would be well to check the thermometer used in the first runs. The catalyst tube was taken out of the large furnace tube and the nitrogen thermometer was inserted half-way through a rubber stopper into the tube. A standard nitrogen thermometer was placed likewise at the other end. The following table indicates the differences found:

Standard thermometer	Furnace thermometer
342°	357°
361	375
378	390
430	420

The temperature of the catalyst itself and the temperature of the thermocouple in contact with the glass touching the catalyst was found to differ also. A thermocouple was imbedded in the pill form of catalyst during short trial run. The temperature inside was 373-375° and the temperature outside was 397-403°.

ANALYSIS

The gas formed from the decomposition of ethyl acetate was analyzed according to the usual methods:

(1) The carbon dioxide was absorbed in 1:1 potassium hydroxide contained in a Hempel single pipette.

(2) Ethylene was absorbed in a saturate bromine solution in a Hempel double pipette. The bromine fumes were removed with potassium hydroxide.

The distillate was analyzed by the standard methods.

(1) Acetic acid: About 2 grams of weighed distillate was mixed with about 100 cc of water and titrated at once with a standard 0.5 N solution of sodium hydroxide.

(2) Ethyl acetate: Fifty cc of potassium hydroxide were placed in pressure flask. About 2 grams of weighed distillate were added. After heating to 100° for an hour and cooling, the solution was titrated with a 0.5 N solution of hydrochloric acid with phenolphthalein. A blank was also run. Proper allowance for free acid was made by titrating a weighed sample before saponifying.

(3) Acetone: Fifty cc of a 0.5 N solution of sodium hydroxide were added to a weighed 0.5 gram sample of distillate. After shaking 5 minutes, a 0.5 N solution of iodine was added slowly until there was a 25 per cent excess. After shaking ten minutes, a sufficient amount of hydrochloric acid was added to neutralize the 50 cc of sodium hydroxide. The excess iodine was titrated with a 0.5 N sodium thiosulphate solution using starch as an indicator.

PREPARATION OF THE CATALYST

Alumina was found by Sabatier to have an activity dependent upon the conditions of preparation. It was believed that alumina prepared by precipitation would be the best.

In runs 1-8 and 10-11 inclusive, the catalyst was prepared according to the following method. A solution of 200 grams of $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 12 \text{H}_2\text{O}$ in 8 liters of distilled water was prepared. There was mixed with the alum solution 200 grams of acid-washed shredded asbestos. After standing

24 hours, the aluminum hydroxide was precipitated with concentrated ammonium hydroxide. The asbestos and aluminum hydroxide was washed by decantation, followed by washing on a filter until no sulphate was detected with Barium chloride in the wash water. After the product was dried at 90-105° in an air oven, it was reshredded.

The catalyst in run 9 was aluminum hydroxide precipitated in the same way as above, but without asbestos. It was powdered in a mortar and sieved. The siftings between 40-mesh and 100-mesh were used.

The catalyst used in the other runs was made by using one mol of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 2 liters of distilled water. Concentrated ammonium hydroxide was added to the boiling solution of nitrate until no further precipitation occurred. After boiling 15 minutes and cooling, the oxide was washed by continuous decantation for several days. The catalyst was dried at 100° and powdered so that the siftings between 40-mesh and 100-mesh could be used in a pill machine. The pills weighed 0.125-0.13 grams each.

The following suggestions may be made in regard to the future work:

(1) The outflow of the salt solution from the gas holder should be regulated to keep a constant gas pressure in the reaction tube.

(2) The receiver for the distillate should allow the liquid to draw off at any time during a run without allowing air to enter.

(3) An apparatus should be devised to produce a constant flow of the vapor of the liquid to be catalyzed into the reaction tube.

CONCLUSIONS

1. The rate of catalytic decomposition of ethyl acetate increases with the temperature of Al_2O_3 .
2. With the rise of temperature the formation of CO_2 increases more rapidly than the formation of ethylene.
3. Al_2O_3 dried at 440° has a comparatively low catalytic efficiency.
4. The activity of Al_2O_3 decreases gradually with the time it is in use as a catalyst.
5. Al_2O_3 prepared by precipitation from a cold solution is more effective as a catalyst than Al_2O_3 prepared from a hot solution. The catalytic activity appears to be dependent upon the porosity of the Al_2O_3 .
6. Acetic acid and alcohol passed over Al_2O_3 at 440° is converted into ethyl acetate with 31 per cent efficiency.
7. Al_2O_3 converts from 40 - 70 per cent of the acetone derived from ethyl acetate into secondary products.

I (a)

No. of tem- per-	Dura- tion of	Kind of Catalyst	No. of Grams of	Amt. of Distil- lata in	Ratio of
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I (a)

No. of of	Tem- pera- ture	Dura- tion	Wt. of Catalyst	Kind of	No. of	Grams of	Amt. of Distillate	Analysis in	Ratio of
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II (a)

To- Ave.	Ave.	Min.	Analysis of Gas Ratio	Weight in
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III (a)

Wt. of Products in Distillate		Ethyl Acetate Equiva-	% Acetone
Wt. of	in Grams	alent of Products	as Com-

I (b)

No. Temp. Dur- Wt. of Kind of No. of Gr. of Ant. of Analysis of Ratio

II (b)

To- Ave.	Ave.	Min.	Analysis of Gas Ratio	Wt. in
tal Amt.	Amt. of	El.	of Eth- Remarks	Grams

III (b)

Wt. of	Wt. of Products in Distil-	Ethyl acetate Equivalent	% Acetone
		as product	as name

I (c)

No. of of	Tem- pera- ture	Dur- ation	Wt. of Cata-	Kind of	No. of Times of	Grams of Distl-	Amt. of Distillate	Analysis of	Ratio of Ace-
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II (c)

Analysis of Gas Ratio			
To- Ave.	Min.	Analysis of Gas	Ratio
tal Amt.	Amt.	Amt. H ₂ O. H ₂ O.	as
			Percent

III (c)

Wt. of Under-	Wt. of Products in Dis- tillate in Grams	Ethyl Acetate Equivalent of Products	% Ace- tone As com-
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